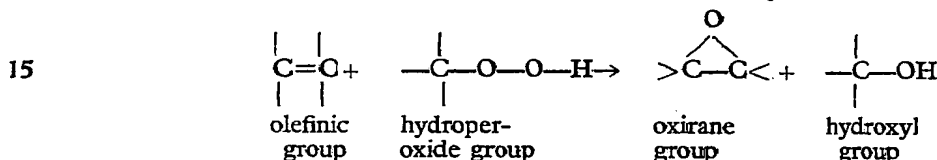# PATENT SPECIFICATION (11) 1249079

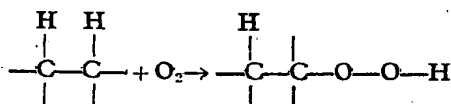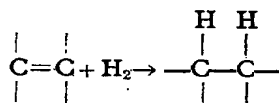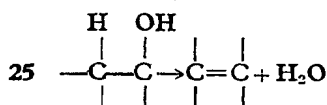## (54) A PROCESS FOR EPOXIDIZING OLEFINS WITH ORGANIC HYDROPEROXIDES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

It is known to convert olefinic compounds into the corresponding oxirane compounds in that they are reacted with an organic hydroperoxide compound according to the following general equation:

$$\begin{matrix}|\ \ |\\ C=C\\ |\ \ |\end{matrix} + \begin{matrix}|\\ -C-O-O-H\\ |\end{matrix} \rightarrow \overset{O}{\overset{\displaystyle \diagup\diagdown}{>C-C<}} + \begin{matrix}|\\ -C-OH\\ |\end{matrix}$$

olefinic group   hydroperoxide group   oxirane group   hydroxyl group

The hydroxyl compound resulting from the reaction may, if so desired, be reconverted into the hydroperoxide compound. When there is a carbon atom, carrying at least one hydrogen atom, adjacent to the carbon atom which carries the hydroxyl group, the regeneration is as a rule most advantageously effected by dehydration, hydrogenation and oxidation as represented by the following reaction scheme:

$$\begin{matrix}H\ \ OH\\ |\ \ \ |\\ -C-C-\\ |\ \ \ |\end{matrix} \rightarrow \begin{matrix}|\ \ |\\ C=C\\ |\ \ |\end{matrix} + H_2O$$

$$\begin{matrix}|\ \ |\\ C=C\\ |\ \ |\end{matrix} + H_2 \rightarrow \begin{matrix}H\ \ H\\ |\ \ \ |\\ -C-C-\\ |\ \ \ |\end{matrix}$$

$$\begin{matrix}H\ \ H\\ |\ \ \ |\\ -C-C-\\ |\ \ \ |\end{matrix} + O_2 \rightarrow \begin{matrix}H\ \ \ \ \ \ \ \ \ \ \\ |\ \ \ |\\ -C-C-O-O-H\\ |\ \ \ |\end{matrix}$$

It is often possible to carry out the first two steps simultaneously.

It will be appreciated that, when the olefinic compound which is an intermediate in the above scheme, is a saleable product, the hydrogenation and oxidation steps may be omitted. If the hydroxyl compound is a saleable product, it may even be attractive to omit the dehydration step.

In general, organic hydroperoxides are prepared, as is well-known to those skilled in the art, by means of an oxidation reaction as represented by the following general equation:

$$RH + O_2 \rightarrow R-O-O-H$$
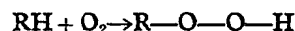
in which R represents a monovalent hydrocarbyl group which may or may not be substituted.

(It will be appreciated that the last step in the above regeneration scheme is covered by the general equation which has just been given).

Preferably, the group R has from 3 to 20 carbon atoms. Most preferably, it is a hydrocarbyl group, in particular a secondary or tertiary alkyl or aralkyl group, having from 3 to 10 carbon atoms. Especially preferred among these groups are the tertiary alkyl and secondary or tertiary aralkyl groups, including, e.g., tertiary butyl, tertiary pentyl, cyclopentyl, 1-phenylethyl-1, 2-phenylpropyl-2 and the various tetralinyl radicals which originate by elimination of a hydrogen atom from the aliphatic side-chain of the tetralin molecule.

Aralkyl hydroperoxide, wherein the hydroperoxy group is linked to that carbon atom of an alkyl side-chain which is attached directly to an aromatic ring, including 1-phenylethyl - 1 - hydroperoxide and 2 - phenylpropyl - 2 - hydroperoxide, are often called after the corresponding hydrocarbons, e.g. ethyl benzene hydroperoxide and cumene hydroperoxide. This practice will also be followed hereinafter. It will be appreciated that, when using ethylbenzene hydroperoxide, the resulting hydroxyl compound is 1 - phenylethanol - 1, also to be called methyl phenyl carbinol, which may be dehydrated to styrene, and that, when using cumene hydroperoxide, the resulting hydroxyl compound is 2-phenylpropanol-2, also to be called dimethyl phenyl carbinol, which may be dehydrated to alpha-methylstyrene. Of course, both styrene and alpha-methylstyrene are industrially useful products, and it may, therefore, well be preferred to use and/or sell them as such, and to refrain from regenerating ethylbenzene and cumene, respectively.

Tertiary amylenes, which are useful as isoprene precursors, may be obtained by dehydration of the alcohol, which is formed when using tertiary pentyl hydroperoxide.

For the sake of brevity the term hydrocarbon will hereinafter generally be employed to denote the compound RH as defined in the above, although, as set out, R may also be a substituted hydrocarbyl group.

The organic hydroperoxide reactant used as a starting material may be in a dilute or concentrated, purified or unpurified condition. It is known that 5 to 70% by weight solutions of the hydroperoxide in the corresponding hydrocarbon may, as a rule, readily be prepared by oxidizing the said corresponding hydrocarbon. Isolation of the organic hydroperoxides becomes more difficult as the volatility of the hydrocarbons decreases and the use of the solutions as such may then become preferable.

Solutions of organic hydroperoxides in the corresponding hydrocarbons, obtained by one of the known oxidation techniques, usually also contain a proportion of the alcohol which is formed by reduction of the organic hydroperoxide, and this alcohol may also be partially oxidized to the corresponding ketone. Thus, a solution of ethylbenzene hydro-
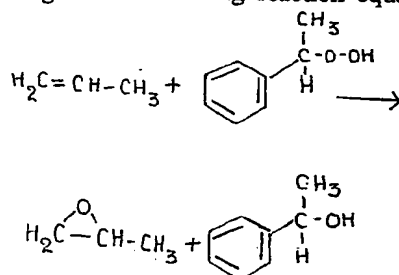
peroxide in ethylbenzene, generally, also contains methyl phenyl carbinol and methyl phenyl ketone. After the reaction with an olefinic compound methyl phenyl ketone may be converted into methyl phenyl carbinol by hydrogenation, and the total amount of methyl phenyl carbinol finally obtained, may be converted into styrene, and, if desired, further converted into ethylbenzene.

In principle, any organic compound having at least one olefinic double bond may be reacted with an organic hydroperoxide in the manner described above. The compounds may be acyclic, monocyclic, bicyclic or polycyclic and they may be mono-olefinic, diolefinic or polyolefinic. If there are more than one olefinic linkages, these may either be conjugated or non-conjugated. Generally preferred are olefinic compounds having from 2 to 60 carbon atoms. Although substituents, which should preferably be relatively stable, may be present, acylic mono-olefinic hydrocarbons having from 2 to 10 carbon atoms are of particular interest. Such hydrocarbons include, e.g., ethylene, propylene, isobutylene, hexene-3, octene-1 and decene-1. Butadiene may be mentioned as an example of a suitable diolefinic hydrocarbon. Substituents, if present, may, e.g., be halogen atoms or comprise atoms of oxygen, sulphur and nitrogen together with atoms of hydrogen and/or carbon. Of particular interest are olefinically unsaturated alcohols, and halogen-substituted olefinically unsaturated hydrocarbons, including, e.g., allyl alcohol, crotyl alcohol and allyl chloride. Particularly preferred are alkenes having from 3 to 40 carbon atoms, which may or may not be substituted with a hydroxy or a halogen atom.

Oxirane compounds are materials of established utility and many are chemicals of commerce, in particular olefin oxides such as, e.g., ethylene oxide and propylene oxide. As, e.g., disclosed in U.S. Patent Specifications Nos. 2,815,543, 2,871,219 and 2,987,498, propylene oxide may be converted into useful polymeric products by polymerization or copolymerization. Of commercial interest is also epichlorohydrin which may be obtained from allyl chloride and may, if so desired, be converted into glycerol. Of course, glycerol may also be made from the oxirane compound which is formed when starting from allyl alcohol.

It is well-known that ethylene oxide is produced on a large scale by reacting ethylene with molecular oxygen using a silver-containing catalyst. Another route to ethylene oxide consists in the addition of hypochloric acid to the double bond, followed by dehydrochlorination. This route has also been found very suitable for the production of propylene oxide. However, the reaction of propylene with a hydroperoxide, discussed in the above, is a highly promising alternative route. Particularly attractive is the epoxidation of propylene with ethylbenzene hydroperoxide

according to the following reaction equation:

$$H_2C=CH-CH_3 \; + \; \underset{H}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{C}}}-O-OH \longrightarrow$$

$$H_2\overset{O}{\overset{\diagdown}{C}}-CH-CH_3 \; + \; \underset{H}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{C}}}-OH$$

propylene oxide   methyl phenyl carbinol

It has already been pointed out above that
styrene may then be obtained as a valuable by-
5 product.

The present invention relates to an improve-
ment of the known process, discussed above,
in which one or more olefinic compounds are
reacted with one or more organic hydro-
10 peroxides so as to produce one or more oxirane
compounds. The improvement consists in the
use of a special type of catalyst. Various
catalysts have been disclosed in prior publica-
tions. For instance, U.S. Patent Specification
15 No. 2,754,325 describes the use in dissolved
condition of heteropoly acids containing transi-
tion metals, such as chromium, molybdenum
and tungsten, and U.S. Patent Specifications
Nos. 3,350,422 and 3,351,635 describe the use
20 of solutions of transition metal compounds (V,
Mo, W, Ti, Nb, Ta, Re, Se, Zr, Te and U).
However, the known catalysts are generally
effective only when homogeneously dispersed
through the reaction mixture. It would, of
25 course, be of advantage if catalysts or catalyst
compositions could be employed, which are
substantially insoluble in the reaction mixture,
because such heterogeneous catalyst systems
can much more easily be separated from the
30 reaction products.

Now, the present invention relates to a
catalyst composition which is essentially in-
soluble in the epoxidation reaction mixture,
thus providing a heterogeneous system. It has
35 surprisingly been found that the catalyst com-
position of the invention is very active, and
leads to high conversions of the organic hydro-
peroxide(s) introduced with high selectivities to
the oxirane compound(s) concerned, these
40 selectivities being defined as the molar ratios
of oxirane compound(s) formed to organic
hydroperoxide(s) converted.

In general, the reaction is conducted in the
liquid phase using solvents and/or diluents
45 which are liquid at reaction temperature and
pressure, and substantially inert to the re-
actants as well as to the products. The presence
of reaction materials such as, e.g., water is
desirably avoided. A substantial part of the
50 solvent may consist of materials present in

the hydroperoxide solution employed. Pre-
ferred solvents further to be added are mono-
nuclear aromatic compounds, e.g., benzene,
toluene, chlorobenzene, bromobenzene, ortho-
dichlorobenzene, and alkanes, e.g. octane, 55
decane and dodecane. However, an excess
amount of the olefinic reactant may also serve
as a solvent together with the solvent material
introduced together with the organic hydro-
peroxide, so that no addition of any further 60
solvents is needed. In most instances, however,
added solvent is used. The total amount of
solvent material may be up to 20 moles per
mole of the hydroperoxide.

The reaction, generally, proceeds at moder- 65
ate temperatures and pressures, in particular
at temperatures in the range of from 0°C to
200°C, the range from 25°C to 200°C being
preferred. The precise pressure is not critical
so long as it suffices to maintain the reaction 70
mixture in a liquid condition. Atmospheric
pressure may be satisfactory. In general, pres-
sures are suitably in the range of from 1 to
100 atm. abs.

At the conclusion of the reaction, the liquid 75
mixture comprising the desired products may
easily be separated from the solid catalyst
material. The liquid mixture may then be
worked up using any suitable conventional
methods, including, e.g., fractional distillation, 80
selective extraction and filtration. The sol-
vent, the catalyst and any unreacted olefin or
hydroperoxide may be recycled for further
utilization. The process of the invention can
successfully be carried out with the catalyst 85
in the form of a slurry, of a moving bed or a
fluidized bed. However, a fixed catalyst bed
would appear preferable for large-scale in-
dustrial operation. The process may be carried
out in a batch-wise manner, but also semi- 90
continuously or continuously. The liquid con-
taining the reactants may then be passed
through the catalyst bed, so that the effluent
from the reaction zone is entirely or at any rate
practically free from catalyst material. 95

The catalyst composition employed accord-
ing to the present invention comprises titanium
in chemical combination with a solid silica
and/or inorganic silicate. The titanium will
during the reaction assume the tetravalent 100
state, and is preferably combined with the solid
silica and/or inorganic silicate in that oxida-
tion state. The proportion of titanium in the
catalyst composition can be vared, but propor-
tions of at least 0.1% by weight of titanium 105
calculated as the dioxide, are as a rule very
satisfactory, proportions of from 0.2% to 50%
by weight, calculated on the same basis, being
preferred. However, still larger proportions of
titanium can be used. 110

Suitable solid silicas and/or inorganic
silicates contain at least 50%, but, preferably,
at least 75% and, most preferably, at least

90% by weight of silicon, calculated as the dioxide, that is silica. Suitably, the solid silicas and/or inorganic silicates are further characterized by having a relatively large specific surface area, in particular a specific surface area of at least 1 m²/g. Preferably, the specific surface area is in the range of from 25 to 800 m²/g.

Suitable is, e.g., synthetic, porous silica in a relatively dense, close-packed form, consisting of particles of amorphous silica flocculated or linked together, including silica gel and precipitated silica. The preparation and properties of such materials are described by R. G. Iler in his book "The Colloid Chemistry of Silica and Silicates", Cornell University Press, New York, 1955, Chapter VI and in U.S. Patent Specification 2,657,149. Among the silica gels which are available commercially, those with a specific surface area in the range of from 25 to 700 m²/g and a pore volume in the range of from 0.3 to 1.3 ml/g, and which consist to at least 99% wt of silica, are generally the most suitable.

Also suitable are, however, synthetic, silica powders consisting of particles of amorphous silica flocculated in openpacked, readily disintegrated, loosely-knit aggregates, such as, e.g., fumed pyrogenic silica obtained by the combustion of hydrogen and oxygen with silicon tetrachloride or tetrafluoride. Such products are commercially produced and sold by various companies, including, e.g., Cabot Corporation ("Cab-O-Sil") and Degussa ("Aerosil"). (The words "Degussa" and "Aerosil" are registered Trade Marks). Among these products those with a specific surface area in the range of from 50 to 400 m²/g and a particle size in the range of from 0.007 to 0.05 micron, and which to at least 99·% consist of silica, are generally the most suitable.

Furthermore, suitable solid silicas and/or inorganic silicates include the crystalline alumino-silicates which are known in the art as molecular sieves, as well as naturally-occurring crystalline mineral silicates, including, e.g., asbestos minerals, e.g., serpentine (hydrous magnesium silicates); clay minerals, e.g., hectorite (magnesium lithium silicate), kaolins and bentonites, and micaceous minerals, e.g., phlogopite (potassium magnesium aluminium silicate) and vermiculite (a hydrous magnesium silicate). Preferred are, however, synthetic amorphous solid silicas and/or inorganic silicates, in particular those which essentially consists of substantially pure silica, e.g., at least 95·% silica.

It may be advantageous to include promoters in the catalysts to be used according to the invention, in particular, compounds of alkaline earth metals, including, e.g., magnesium, calcium, strontium and barium. Preferred are the oxides and such comounds as are readily convertible into oxides. For effect-

ing this conversion a pretreatment of the initially prepared catalyst composition prior to its use may be desirable. The proportions of the promoter or promoters are not critical, but proportions exceeding 10% by weight, calculated as metal on the catalyst support, are not as a rule required. The inclusion of promoters is especially advantageous when employing solid silicas and/or inorganic silicates with strongly acidic sites, e.g., when the intrinsic acidity is less than −3. The intrinsic acidity, generally represented by pK_a, is determined by titration of the material concerned with an appropriate base in the presence of dye indicators, as disclosed, for example, in U.S. Patent Specification No. 2,868,688.

The catalyst compositions to be used according to the present invention may be prepared by such conventional techniques as, e.g., dry-mixing followed by calcination, co-gellation, co-precipitation, impregnation and ion-exchange. For example, a mixture of a titanium salt and a silica sol may be co-gelled, the material then being dried and ground to an appropriate size. Alternatively, the co-gelled material may be slurried and spray-dried. However, the catalyst composition may, e.g., also be prepared by reacting the hydroxyl groups at the surface of a solid silica and/or inorganic silicate with a titanium salt by the procedure disclosed in U.S. Patent Specification No. 3,116,542, 3,270,459 or 3,274,120. In yet another technique, a fumed pyrogenic catalyst composition, in particular a pyrogenic titania-silica composition is prepared by the combustion of hydrogen and oxygen with a mixture of a silicon tetrahalide and a titanium halide.

The catalyst composition may be subjected to a pretreatment prior to utilization in the process. As a rule it is preferable to do so in order to obtain a higher activity. As a rule the pretreatment suitably consists in heating the catalyst composition in an atmosphere of a non-reducing gas, such as, e.g., nitrogen, argon, carbon dioxide or of an oxygen-containing gas, such as, e.g., air. However, the most suitable method of pretreatment in general also depends upon the form of chemical combination in which the titanium component is provided. In many instances titanium compounds have to be converted into oxide, for example, if the catalyst compositions initially contain titanium in the form of its tetrachloride or as a mixture of tetra-kismethylpropylaminotitanium and KCl. The conversion may as a rule suitably be effected by heating in a non-reducing atmosphere, in particular at temperatures in the range of from 350°C to 800°C during times in the range of from 1 to 18 hours.

The catalyst compositions to be used according to the present invention may be employed in any convenient physical form, for example,

in the form of a powder, as well as of flakes, spheres or pellets.

The catalyst compositions to be used according to the invention may also comprise other components which are inert to the reactants and products. Other substances known to catalyze the epoxidation reaction may be present in combination with the catalysts of the present invention, provided the catalytic activity is not reduced by the combination. Generally, the catalysts of the present invention may additionally comprise up to 10% by weight of the oxides or hydroxides of boron, tin, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, uranium, bismuth and rare earth elements having atomic numbers of from 57 to 71 inclusive.

EXAMPLE I

Five catalyst compositions according to the present invention (A₁, A₂, A₃, B, C) were prepared and tested. For comparison, three further catalyst compositions, not in accordance with the present invention, (D, E, F) were also tested.

Titanium on silica catalyst from pyrogenic silica and TiCl₄

Catalyst A₁ was prepared in the following manner.

A mixture of 25 g of pyrogenic silica having a specific surface area of 390 m^2/g (Cabot Corporation grade EH—5 Cab-O-Sil) and 1700 ml of n-heptane was dried by heating at reflux in a glass reactor equipped with a Dean Stark trap (to collect water-heptane azeotrope) for a period of 19 hours. After cooling to approximately 25°C, a 0.47 g (2.5 millimoles) sample of titanium tetrachloride was added to the reactor, and the reaction mixture heated to 97°C, hydrogen chloride being evolved, removed by a stream of dry nitrogen and passed into a scrubber containing dilute caustic. When approximately 2.5 millimoles (one equivalent based on TiCl₄) of hydrogen chloride had evolved, approximately 10 ml of water was added in approximately 0.5 ml portions to initiate the evolution of additional hydrogen chloride. After a reaction time of approximately 16 hours at 97°C the evolution of hydrogen chloride stopped entirely. The reaction mixture was then evaporated under reduced pressure at elevated temperature, and the silica residue dried overnight at a temperature of 120°C and a pressure of 180 mm Hg. The resulting product contained 0.4% by weight of the element titanium.

Catalyst A₂ was prepared in the same manner as catalyst A₁, but the amount of TiCl₄ added was 4.68 g, so that the product contained 4% by weight of the element titanium.

Catalyst A₃ was prepared in a manner similar to that used for catalyst A₁, except that titanium trichloride was added instead of titanium tetrachloride. The amount of titanium trichloride added was 3.62 g (0.023 mole). Addition of water was commenced when approximately 0.023 mole of hydrogen chloride (one equivalent based on TiCl₃) had been evolved. The resulting product contained 4.2% by weight of the element titanium.

Silicon on titania catalyst from pyrogenic titania and SiCl₄

Catalyst B was prepared in the following manner.

A mixture of 25 g of pyrogenic titania having a specific surface area of approximately 50 m^2/g and a particle size of 15—40 millimicrons (Degussa Inc. grade P—25 titanium dioxide) and 1700 ml of n-heptane was refluxed in a glass reactor equipped with a Dean Stark trap (to collect water-heptane azeotrope) for a period of 19 hours. After cooling to room temperature a 7.84 g (0.046 mole) sample of silicon tetrachloride in 25 ml of dry n-heptane was added to the reactor, and the reaction mixture heated at 97°C until approximately 0.046 mole of hydrogen chloride had evolved. The evolved hydrogen chloride was removed from the glass reactor into a scrubber of dilute caustic. Approximately 10 ml of water was then added in approximately 0.5 portions to initiate evolution of additional hydrogen chloride. When after a reaction time of approximately 20 hours at 97°C the evolution of hydrogen chloride had stopped entirely, the reaction mixture was evaporated at approximately 100°C under reduced pressure, and the residue dried at a temperature of 120°C and a pressure of 180 mm Hg for 16 hours. The resulting product contained 3.2% by weight of the element silicon.

Silica-titania catalyst from pyrogenic silica and pyrogenic titania

Catalyst C was prepared in the following manner.

A mixture of 3 g pyrogenic silica (Cabot Corporation grade EH—5 Cab-O-Sil) and 1 g of pyrogenic titania (Degussa Inc. grade P—25 titanium dioxide) was intimately mixed and then heated in a furnace at 700°C for 24 hours. The resulting product was powdered by grinding.

Titania catalyst without silicon

Catalyst D was a commercially available pyrogenic titania (Degussa Inc. grade P—25 titanium dioxide).

Silica catalyst without titanium

Catalyst E was a commercially available pyrogenic silica (Cabot Corporation EH—5 Cab-O-Sil).

Physical mixture of pyrogenic silica and titania

Catalyst F was a physical mixture consisting of 0.75 g of pyrogenic silica (EH—5 Cab-O-Sil) and 0.25 g of pyrogenic titania (Degussa, P—25).

In a series of experiments a 1 g sample of

each of the catalyst compositions was contacted with 36.5 g of 1-octene and 4.5 g of t-butyl hydroperoxide, and in the case of the catalysts A$_2$ and A$_3$ also 2.1 g of nonane as a diluent, in a 100 ml glass reactor. The reaction conditions, the hydroperoxide conversion and the yield of 1-octene oxide with respect to hydroperoxide converted are shown in Table I.

TABLE I

Catalyst	Reaction time, hr.	Temp. °C.	Hydroperoxide conversion %	Epoxide selectivity %
A$_1$	4	107	82.3	97.3
A$_2$	1	107	86	90
A$_3$	2.25	106	64.7	93.8
B	21	109	33.1	81
C	10	110	85	91
D	18	110	90	0
E	20	110	37.8	10.3
F	24	110	39	0

After completion of the reaction with catalyst A$_2$, the catalyst was removed from the reaction mixture by filtration. Colorimetric analysis of the reaction mixture filtrate showed the presence of less than 0.4 parts per million of titanium in solution.

EXAMPLE II

Four catalyst compositions according to the present invention (A, B, C, D) were prepared and tested. For comparison, two further compositions, not in accordance with the present invention, (E, F) were also tested.

Titania and silica in approximately equal molar proportions from SiCl$_4$ and TiCl$_4$

Catalyst A was prepared in the following manner.

A mixture of 32.86 g of silicon tetrachloride (Matheson, Coleman and Bell semi-conductor grade) and 27.96 g of titanium tetrachloride was added dropwise to 550 ml of deionized water at a temperature between 25°C and 40°C. The resulting mixture was evaporated on a steam bath under reduced pressure and the residue dried at a temperature of 150°C overnight. The product contained 48.6% by weight of the element titanium.

Titanium on silica from SiCl$_4$ and TiCl$_4$

Catalyst B was prepared by a procedure similar to that used for catalyst A. A composition containing 3.9% by weight of the element titanium, was prepared starting from a mixture of 25 ml of silicon tetrachloride and 2.8 g of titanium tetrachloride which was contacted with 500 ml of deionized water.

Titanium on silica from SiCl$_4$ and TiCl$_4$

Catalyst C was prepared by a procedure similar to that used for catalyst A. A composition containing 1.9% by weight of the element titanium, was prepared starting from a mixture of 36.5 g of silicon tetrachloride and 0.82 g of titanium tetrachloride which was contacted with 500 ml of deionized water.

Titania on silica from SiCl$_4$ and TiCl$_4$.

Catalyst D was prepared by a procedure similar to that used for catalyst A. A composition containing 0.3% by weight of the element titanium, was prepared starting from a mixture of 36.5 g of silicon tetrachloride and 0.08 g of titanium tetrachloride which was contacted with 500 ml of deionized water.

Titania catalyst (without silicon) from TiCl$_4$.

Catalyst E was prepared in the following manner.

A 43 g sample of titanium tetrachloride was added dropwise to 500 ml of deionized water over a period of 15 minutes. The resulting mixture was evaporated on a steam bath and the titania residue was dried at a temperature of 120°C under a pressure of 180 mm Hg for 20 hours. The product contained 60% by weight of the element titanium.

Silica catalyst without titanium

Catalyst F was prepared in the following manner.

A 25 ml sample of silicon tetrachloride

(Matheson, Coleman and Bell, semi-conductor grade) was added dropwise over a period of 20 minutes to 500 ml of deionized water. The resulting mixture was evaporated on a steam bath under reduced pressure and the silica residue dried overnight at a temperature of 120°C and a pressure of 180 mm Hg. Analysis showed that the silica product contained less than 35 ppm by weight of titanium.

In a series of experiments a 1 g sample of each of the catalyst compositions was contacted with 36.5 g of 1-octene and 4.5 g of t-butylhydroperoxide in 2.1 g of nonane as a diluent in a 100 ml glass reactor. The reaction conditions and results are shown in Table II.

TABLE II

Catalyst	Temp., °C.	Reaction time, hr.	Hydroperoxide conversion	Epoxide selectivity
A	111	4.5	61	84
B	106	2.5	73.8	92.2
C	105	3	75	87.2
D	103	5	61.3	88
E	113	21	73.1	9.2
F	107	20	35	27

EXAMPLE III

Two catalysts were prepared using substantially the same technique as for the preparation of the catalysts A_1 and A_2 of Example I. However, the silica was replaced by other inorganic siliceous solids. The catalysts were also tested in the same manner as the catalysts A_2 and A_3 of Example I. The reaction conditions and results are shown in Table III.

Titanium on clay

Catalyst composition A containing 4.4% by weight of the element titanium was prepared from 4.68 g of titanium tetrachloride with 25 g of azeotropically dried Higlo 50 clay (marketed by Georgia Kaolin).

Titanium on magnesium silicate

Catalyst composition B containing 3.7% by weight of the element titanium was prepared from 4.6 g of titanium tetrachloride and 25 g azeotropically dried magnesium silicate gel (10.2 wt Mg and 35.6 wt Si; magnesia-silicate marketed by the Floridin Co.).

TABLE III

Catalyst	Temp., °C.	Reaction time, hr.	Hydroperoxide conversion	Epoxide selectivity
A	103	3	78	77
B	110	3	72.3	87.5

EXAMPLE IV

Four catalysts were prepared using substantially the same technique as for the preparation of the catalysts A_1, A_2 and A_3 of Example I. However, other metals were incorporated besides titanium. The catalysts were tested in the same manner as the catalysts A_2 and A_3 of Example I. The reaction conditions and results are shown in Table IV.

Titanium and zirconium on silica

Catalyst composition A containing 2.9% by weight of the element titanium and 0.5% by weight of the element zirconium was prepared from 1.3 g of zirconium tetrachloride and 1.7 g of titanium tetrachloride with 25 g of azeotropically dried commercial pyrogenic silica. First only the zirconium tetrachloride was added, and when one equivalent of HCl

(based on ZrCl$_4$ charged) was evolved, the titanium tetrachloride was added, the usual procedure then further being applied.

Titanium and niobium on silica

5   Catalyst composition B containing 3.3% by weight of the element titanium and 0.4% by weight of the element niobium was prepared from 1.4 g of NbCl$_5$ and 1.7 g of TiCl$_4$ with 25 g of azeotropically dried pyrogenic 10 silica using substantially the same technique as employed for catalyst A.

Titanium and boron on silica

Catalyst composition C containing 1.6% by weight of the element titanium and 0.2% by 15 weight of the element boron was prepared

from 3.4 g of boron trichloride and 2.4 g of titanium tetrachloride with 25 g of azeotropically dried pyrogenic silica, using substantially the same technique as employed for catalysts A and B.   20

Titanium and tin on silica

Catalyst composition D containing 2.4% by weight of the element titanium and 1.1% by weight of the element tin was prepared from 2.4 g of titanium tetrachloride and 0.45 25 g of stannic tetrachloride with 25 g of azeotropically dried pyrogenic silica, using substantially the same technique as employed for catalysts A, B and C.

TABLE IV

Catalyst	Temp., °C.	Reaction time, hr.	Hydroperoxide conversion	Epoxide selectivity
A	106	0.5	77	91
B	110	0.5	69	86
C	105	17	99	79
D	106	4.5	75	85

EXAMPLE V

Six catalyst compositions (A, B, C, D, E, F) were prepared and subjected to a calcination treatment prior to use. They were then 35 tested by contacting a sample (0.5 g for A, B and D; 1 g for C, E and F) with 1-octene (42 g for A, B and C; 30 g for D; 36.5 g for E and F) and t-butyl-hydroperoxide (5.5 g for A, B and C; 4 g for D; 4.5 g for E and F 40 in a 100 ml glass reactor. The reaction mixture also contained 16 g of n-hexane as a diluent in the case of catalyst D. The reaction conditions and results are shown in Table V.

Catalyst A. Titanium on silica

45   A 20 g sample of commercial silica gel having a specific surface area of 340 m^2/g and a pore volume of 1.15 cc/g (Davison grade 62 silica gel preheated at 500° for 2 hours) was contacted with a solution of 2 ml 50 of titanium tetrachloride in 26 ml of 1.72N hydrochloric acid at a temperature of 25°C. The impregnated silica gel was pre-dried in a steam bath and then contacted with 15 ml of 8N nitric acid at a temperature of 25°C. The 55 liquid components were evaporated on a steam bath. The residue was dried at a temperature of 150°C for 3 hours and then calcined at a temperature of 800°C for 2 hours. The resulting composition contained 4.4% by weight of 60 the element titanium.

Catalyst B. Titanium on silica

A 20 g sample of commercial silica gel having a specific surface area of 340m^2/g and a pore volume of 1.15 cc/g was contacted with a solution of 1 ml of titanium tetrachloride in 65 24 ml of 1.72N hydrochloric acid and approximately 1 ml of a 50% wt aqueous solution of hydrogen peroxide. The impregnated silica gel was dried on a steam bath at a temperature of 150°C and then calcined at a tem- 70 perature of 500°C for 2 hours. The resulting product contained 2.2% by weight of the element titanium.

Catalyst C. Titanium on magnesium silicate

A 20 g sample of commercial magnesium 75 silicate gel (10.2% wt Mg and 35.6% wt Si; "Florisil" marketed by the Floridin Co.) having a pore volume of 1.1 cc/g was contacted with a solution of 1 ml of titanium tetrachloride, 4 ml 16N nitric acid, 1 ml of a 50% 80 wt aqueous solution of hydrogen peroxide and 10 ml of water. ("Florosil" is a registered Trade Mark). The impregnated magnesium silicate gel was dried at 150°C and then calcined at 500°C for 2 hours. The resulting 85 composition contained 2.8% by weight of the element titanium.

Catalyst D. Titanium and "didymium" on silica

A 20 g sample of commercial silica gel hav- 90

ing a surface area of 340 m²/g and a pore volume of 1.15 cc/g was contacted with a solution of 2 ml titanium tetrachloride, 2.63 g of didymium nitrate (commercial didymium, that is a complex mixture of rare earth metals), 26 ml of 1.72N hydrochloric acid and 5 ml of a 50% wt aqueous solution of hydrogen peroxide. The resulting mixture was evaporated on a steam bath, dried at a temperature of 150°C and then calcined at a temperature of 500°C for 2 hours. The resulting product contained 4.4% by weight of the element titanium and 4.3% by weight of "didymium" metal.

Catalyst E. Titanium and molybdenum on silica

A 20 g sample of commercial silica gel having a specific surface area of 340 m²/g and a pore volume of 1.15 cc/g was contacted with a solution of 1.73 g of titanium tetrachloride, 0.441 g of ammonium paramolybdate [(NH₄)₆Mo₇O₂₄.4H₂O], 20 ml of 9N nitric acid and 4 ml of a 50% w aqueous solution of hydrogen peroxide. The impregnated silica gel was dried at 150°C and then calcined at 500°C for 2 hours. The resulting composition contained 2.2% by weight of the element titanium and 1.2% by weight of the element molybdenum.

Catalyst F. Titanium, molybdenum and "didymium" on silica

A 20 g sample of commercial silica gel having a specific surface area of 340 m²/g and a pore volume of 1.15 cc/g was contacted with a solution of 1.73 g of titanium tetrachloride, 0.883 g of ammonium paramolybdate [(NH₄)₆Mo₇O₂₄.4H₂O], 1.75 g of didymium nitrate (commercial didymium, a complex mixture of rare earth metals), 20 ml of 4N nitric acid and 4 ml of a 50% w aqueous solution of hydrogen peroxide. The impregnated silica gel was dried at 150°C and then calcined at 500C for 2 hours. The resulting composition contained 2.2% by weight of the element titanium, 2.4% by weight of the element molybdenum and 2.9% by weight of "didymium" metal.

TABLE V

Catalyst	Reaction time, hr.	Temp., °C.	Hydroperoxide conversion, %	Epoxide selectivity, %
A	1	107	56.5	91.2
B	1	107	62.2	86
C	4	110	40	83.4
D	1	88	11	91.6
E	1	105	90	83
F	3/4	104	89	83

EXAMPLE VI

Titanium on silica for various olefins

The olefinic compounds were epoxidized with titania-silica catalysts in glass reactor under the reaction conditions tabulated in Table VI. In Runs 1—11 the catalyst employed was a pyrogenic silica containing 0.3% by weight of titanium (produced by the flame hydrolysis of SiCl₄ and TiCl₄). In Runs 12 and 13 catalysts A₂ of Example I was employed.

TABLE VI

Run	Olefin	Olefin, g	Catalyst, g	Hydroperoxide g	Diluent	Temp., °C.	Reaction, time, hr.	Hydro-peroxide conversion %	Epoxide selectivity %
1	1-Octene	52.5	1	Ethylbenzene (3.1 g)	Ethylbenzene (18 g)	110	17	99	82
2	1-Octene	36.5	1	Cumene (7 g)	Cumene (1 g)	110	20	84.3	72.3
3	1-Octene	73	2	t-Butyl (9 g)	Nonane (2.1 g)	110	3	76.8	99
4	Isobutylene	6	1	t-Butyl (4.5 g)	o-Dichlorobenzene (20 ml)	112	1	44.8	86.8
5	Cyclohexene	40	1	t-Butyl (4.5 g)	—	85	3	43.2	98.5
6	Cyclohexene	28	1	Cyclohexene (15 g)	—	85	2	94	95
7	4-Cyanocyclohexene	20	0.5	t-Butyl (2.3 g)	—	110	6	90	96.5
8	Cyclohexen-3-ol	5	2	t-Butyl (9 g)	o-Dichlorobenzene (40 ml)	110	20	84	85
9	1,2,5,6-Tetra-hydrobenzaldehyde	50	1	t-Butyl (4.5 g)	—	105	3	59	36
10	Mesityl oxide	50	1	t-Butyl (4.5 g)	—	105	3.5	68.7	52.6
11	Methyl β,β'-di-methyl acrylate	25	0.5	t-Butyl (4.5 g)	—	110	20	55	87
12	Allyl chloride	18.5	1	t-Butyl (4.6 g)	—	110	2.2	49	74
13	Allyl alcohol	29	1	t-Butyl (4.5 g)	—	98	3	32	71

EXAMPLE VII

Propylene with ethylbenzene hydroperoxide and titanium on silica catalyst

The catalyst employed was prepared in the following manner.

A 60 g sample of commercial silica gel having a surface area of 340 m²/g and a pore volume of 1.15 cc/g (Davison grade 59 silica) was contacted with a solution of 5.18 g of titanium tetrachloride in 68 ml of 4N nitric acid and 4 ml of 50% wt hydrogen peroxide. The impregnated silica gel was dried at a temperature of 100°C and then calcined at a temperature of 800°C for 2 hours. Analysis of the resulting titania-silica product showed 2.18% by weight of titanium.

The epoxidation of propylene with ethylbenzene hydroperoxide was conducted in 0.5 inch diameter, 6 feet long fixed bed tubular reactor packed with the catalyst. A reaction mixture consisting of 6 moles of propylene per mole of ethylbenzene hydroperoxide in ethylbenzene was continuously fed to the reactor maintained at the indicated temperature and a pressure of 600 psig for a residence time of about 24 minutes. The reaction conditions and the analysis of the product mixture after the indicated reaction time are provided in Table VII.

TABLE VII

Cumulative hours	Temp. °C.	Hydroperoxide conversion, %	Propylene oxide selectivity, %
44	100	76.8	84.0
83	110	89.0	85.0
310	110	85.2	83.0
379	114	87.6	86.5

EXAMPLE VIII

Titanium and other metals on non-siliceous supports. (For comparison)

A number of compositions consisting of various metals, including titanium, supported on silica-free supports were tested as catalysts for the epoxidation of 1-octene with t-butyl hydroperoxide (TBHP). The reaction conditions and results are shown in Table VIII. In runs A—G the catalyst compositions were prepared by reacting a metal halide with either pyrogenic alumina having a specific surface area of 100 m²/g, or Mg(OH)Cl having a specific surface area of approximately 20 m²/g, or zirconia having a specific surface area of 169 m²/g by a procedure similar to that used for preparing catalyst A of Example I. In run H a commercial composition, comprising 2.5% w of the element cobalt and 9.5% w of the element molybdenum on alumina as the support material, marketed by American Cyanamid was employed. In run I the epoxidation of 1-octene with t-butyl-hydroperoxide was conducted in the absence of any catalyst.

TABLE VIII

Run	Ingredients in catalyst preparation	Catalyst, metal on support, % w	Catalyst g	Octene-1, g	TBHP, g	Nonane diluent, g	Temp., °C.	Reaction time, hr.	Hydroperoxide conversion	Epoxide selectivity
A	$TiCl_4$ (1 g) and Al_2O_3 (25 g)	1.2% Ti	1	36.5	9.5	2.1	110	23	69	13
B	$TiCl_4$ (5 g) and Al_2O_3 (25 g)	4.4% Ti	1	36.5	4.5	2.1	110	23	74	13
C	$TiCl_4$ (4.7 g) and ZrO_2 (25 g)	3.5% Ti	1	36.5	4.5	2.1	111	5	24	18
D	$TiCl_4$ (2.3 g) and Mg(OH)Cl (12.7 g)	2.9% Ti	1	36.5	4.5	2.1	110	4.5	60.2	6
E	$NbCl_5$ (3.8 g) and Al_2O_3 (25 g)	5% Nb	1	36.5	4.5	0	110	22	55	7
F	$TaCl_5$ (5 g) and Al_2O_3 (25 g)	5% Ta	1	36.5	4.5	0	110	23	63	0
G	$ZrCl_4$ (2.9 g) and Al_2O_3 (25 g)	2.5% Zr	1	36.5	4.5	2.1	110	11	45	1
H	Co and Mo with Al_2O_3	{2.5% Co, 9.5% Mo}	1	42	5.5	0	110	2	70.2	21
I	None	—	0	36.5	4.5	2.1	110	20	17	13

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EXAMPLE IX
Metals other than titanium on silica. (For comparison)

A number of compositions, consisting of metals other than titanium supported on silica, were tested as catalysts for the epoxidation of 1-octene with t-butylhydroperoxide (TBHP). The reaction conditions and results are shown in Table IX. In Runs A—C the catalyst compositions were prepared by reacting a metal halide with a commercial pyrogenic silica (Cabot Corporation EH—5 Cab-O-Sil) by a procedure similar to that used for catalyst A of Example I. In Runs D—I, the catalyst compositions were prepared by the cohydrolysis of a metal halide and silicon tetrachloride by a procedure similar to that described in Example II. In Run J, the catalyst composition was prepared by contacting a 50 g sample of commercial silica gel having a specific surface area of 750 m^2/g with a solution of 0.625 g chromium trioxide in 20 ml of water, drying the impregnated silica gel at 150°C and then calcining at 500°C for 2 hours. In Run K, the catalyst composition was prepared by contacting a 20 g sample of commercial magnesium silicate gel (10.2%w of the element magnesium and 35.6%w of the element silicon) having a pore volume of approximately 1.1 cc/g with a solution of 0.1 g chromium trioxide in 25 ml of water, drying the impregnated magnesium silicate gel at 150°C and then calcining at 500°C overnight. In Run L, the catalyst composition was prepared by contacting a 10 g sample of commercial pyrogenic silica having a specific surface area of 200 m^2/g (Cabot Corporation grade MS/7 Cab-O-Sil) with a solution of 0.308 g tungstic acid (H$_2$WO$_4$), 45 ml of 25%wt ammonium hydroxide and 5 ml of a 50%wt aqueous solution of hydrogen peroxide, drying the impregnated silica at 150°C and then calcining at 800°C for 2 hours. In Run M, the catalyst composition was prepared by contacting 10 g of commercial pyrogenic silica with a solution of 1 g of rhenic acid (HReO$_4$) in 30 ml of water and subsequently drying at 200°C.

TABLE IX

Run	Catalyst prepared from	Composition of catalyst, % wt (of metal added)	Amount of catalyst, g	Octene-1, g	TBHP g	Nonane diluent, g	Temp., °C.	Reaction time hr.	Hydroperoxide conversion	Epoxide selectivity
A	WCl$_6$ (2.3 g) and SiO$_2$ (25 g)	3.8% W	1	36.5	4.5	2.1	105	18	38.6	25.2
B	NbCl$_5$ (3.8 g) and SiO$_2$ (25 g)	5% Nb	1	36.5	4.5	2.1	108	13	60	1
C	TaCl$_5$ (3 g) and SiO$_2$ (25 g)	5% Ta	1	36.5	4.5	2.1	110	6 1/2	40	32
D	NbCl$_5$ (0.9 g) and SiCl$_4$ (36.7 g)	1.4% Nb	1	36.5	4.5	2.1	110	7	50	5
E	NbCl$_5$ (0.08 g) and SiCl$_4$ (36.7 g)	0.2% Nb	1	36.5	4.5	2.1	103	21	39.7	19.8
F	WCl$_6$ (0.65 g) and SiCl$_4$ (36.9 g)	1.5% W	1	36.5	4.5	2.1	110	70	29	10
G	WCl$_6$ (0.07 g) and SiCl$_4$ (36.7 g)	0.3% W	1	36.5	4.5	2.1	110	70	34	14
H	TaCl$_5$ (0.6 g) and SiCl$_4$ (36.7 g)	3.1% Ta	1	36.5	4.5	2.1	108	20	53.6	7
I	TaCl$_5$ (0.06 g) and SiCl$_4$ (36.6 g)	0.26% Ta	1	36.5	4.5	2.1	111	20	45.4	14.4
J	CrO$_3$ and SiO$_2$	1.3% Cr	1	35	7.5	0	110	1	76	15
K	CrO$_3$ and MgO.SiO$_2$	0.5% Cr	1	42	4.5	0	110	4	39	18
L	H$_2$WO$_4$ and SiO$_2$	2.9% W	1	42	5.5	0	110	4	26.2	37.2
M	HReO$_4$ and SiO$_2$	6.9% Re	1	36.5	4.5	0	105	1	100	0

EXAMPLE X
Various metal compounds without siliceous material (for comparison)

In a series of experiments a variety of metal compounds were tested as heterogeneous catalysts for the epoxidation of 1-octene with t-butylhydroperoxide. In each experiment a 1 g sample of the metal compound concerned was contacted with from 36.5 to 42 g of 1-octene and from 4.5 to 5.5 g of t-butylhydroperoxide. The reaction conditions and results are provided in Table X.

TABLE X

Run	Catalyst	Nonane diluent, g	Reaction time, hr.	Temp., °C.	Hydroperoxide conversion, %	Epoxide selectivity, %
A	TiO_2 (Cabot Corp.)	2.1	20	110	50	0
B	TiO_2 (Degussa, Inc.)	2.1	18	110	40	0
C	TiO_2 (hydrolyzed $TiCl_4$) of Example II E	2.1	21	113	73.1	9.2
D	$Bi_2Ti_2O_7$	0	4	110	48	6
E	$MgTiO_3$	2.1	12	116	28	1
F	$SrTiO_3$	2.1	16	111	35	1
G	$CaTiO_3$	2.1	16	110	28	1
H	ZrO_2	2.1	20	107	76.7	5
I	$(NH_4)_4ZrF_6$	0	2	110	24	0
J	ZrB_2	0	2	110	85	0
K	$CaZrO_3$	0	2	110	10	0
L	Nb_2O_5	0	4.5	115	9	0
M	Ta_2O_5	0	4.5	110	11	5
N	CrO_3	0	0.5	108	99	22
O	$CrCl_3$	0	1.5	96	98	0
P	WC	2.1	112	116	56	5
Q	WO_3	0	22	111	85	8
R	Re_2O_7	0	4	110	100	0
S	TeO_2	0	22	110	33	7
T	SeO_2	0	3	110	97	0
U	UO_2	0	20	110	55	5

EXAMPLE XI

Titanium on silica-alumina

Three catalyst compositions (A, B, C) were prepared and tested in that a 1 g sample was contacted with 17 g of 1-octene, 25 g of ethylbenzene hydroperoxide (added as a 14.2% wt solution in ethylbenzene) and 8 g of nonane in a 100 ml glass reactor at 125°C for 1.5 hours. The results are shown in Table XI.

Catalyst A was prepared in the following manner.

A 210 g sample of commercial silica-alumina (largely consisting of aluminium silicate) having a pKa of −5, a specific surface area of 300 m²/g and a pore volume of 0.75 cc/g (Chemetron Chemicals; 97.6% SiO₂ and 1.2% Al₂O₃) was contacted with a solution of 10 ml of titanium tetrachloride, 144 ml of 4N nitric acid and 18 ml of a 50% wt aqueous solution of hydrogen peroxide. The impregnated silica-alumina was dried at 150°C and then calcined at 800°C for 2 hours. The resulting composition contained 2.2% by weight of the element titanium.

Titanium and magnesium on silica-alumina

Catalyst B was prepared in the following manner.

A 20 g sample of the same commercial silica-alumina as employed for catalyst A was contacted with a mixture of 1 ml titanium tetrachloride, 2.31 g of magnesium nitrate hexahydrate, 19 ml of 4H nitric acid and 1 ml of a 50% wt aqueous solution of hydrogen peroxide. The impregnated silica-alumina was dried at 160°C and then calcined at 800°C for 2 hours. The resulting composition contained 2.2% by weight of the element titanium and 1.1% by weight of the element magnesium and had a pKa of 3.3.

Titanium and calcium on silica-alumina

Catalyst C was prepared in the following manner.

A 20 g sample of the same commercial silica-alumina as employed for catalysts A and B was contacted with a mixture of 1 ml of titanium tetrachloride, 2.12 g of calcium nitrate tetrahydrate, 19 ml of 4N nitric acid and 1 ml of a 50% wt solution of hydrogen peroxide. The impregnated silica-alumina was dried at 160°C and then calcined at 800°C for 2 hours. The resulting product contained 2.2% by weight of the element titanium and 1.8% by weight of the element calcium and had a pKa of 1.5.

TABLE XI

Run	Catalyst	Hydroperoxide conversion, %	Epoxide selectivity, %
A	2.2% w Ti on $SiO_2.Al_2O_3$	74.1	29.1
B	2.2% w Ti/1.1% w Mg on $SiO_2.Al_2O_3$	80.9	72.7
C	2.2% w Ti/1.8% w Ca on $SiO_2.Al_2O_3$	93.3	66.3

WHAT WE CLAIM IS:—

1. An improved process for reacting one or more olefinic compounds with one or more organic hydroperoxides so as to produce one or more oxirane compounds, characterized by the use of a catalyst composition which is essentially insoluble in the reaction mixture, thus providing a heterogeneous system, the said catalyst composition comprising titanium in chemical combination with a solid silica and/or inorganic silicate.

2. A process as claimed in claim 1, characterized in that the proportion of titanium in the catalyst composition, calculated as titanium dioxide, is in the range of from 0.2 to 50% by weight.

3. A process as claimed in claim 1 or 2, characterized in that the solid silica and/or inorganic silicate contains at least 50% by weight of silicon, calculated as silicon dioxide.

4. A process as claimed in claim 3 characterized in that the solid silica and/or inorganic silicate contains at least 75% by weight of silicon, calculated as silicon dioxide.

5. A process as claimed in claim 4, characterized in that the solid silica and/or inorganic silicate contains at least 90% by weight of silicon, calculated as silicon dioxide.

6. A process as claimed in any one of the preceding claims, characterized in that the solid silica and/or inorganic silicate has a specific surface area of at least 1 m²/g.

7. A process as claimed in claim 6, characterized in that the solid silica and/or inorganic silicate has a specific surface area of from 25 to 800 m²/g.

8. A process as claimed in any one of the preceding claims, characterized in that the reaction is carried out at a temperature in the range of from 0°C to 200°C.

9. A process as claimed in claim 8, characterized in that the reaction is carried out at a temperature of from 25°C to 200°C.

10. A process as claimed in any one of the

preceding claims, characterized in that the olefinically unsaturated compound has from 2 to 60 carbon atoms.

11. A process as claimed in claim 10, characterized in that the olefinically unsaturated compound is an alkene of from 3 to 40 carbon atoms, which may or may not be substituted with a hydroxyl group or a halogen atom.

12. A process as claimed in claim 11, characterized in that the olefinically unsaturated compound is propylene.

13. A process as claimed in claim 11, characterized in that the olefinically unsaturated compound is allyl chloride.

14. A process as claimed in claim 11, characterized in that the olefinically unsaturated compound is allyl alcohol.

15. A process as claimed in any one of the preceding claims, characterized in that the organic hydroperoxide is a hydrocarbon hydroperoxide of from 3 to 20 carbon atoms.

16. A process as claimed in claim 15, characterized in that the organic hydroperoxide is tertiary butylhydroperoxide.

17. A process as claimed in claim 15, characterized in that the organic hydroperoxide is an aralkyl hydroperoxide wherein the hydroperoxy group is on a carbon atom attached directly to an aromatic ring.

18. A process as claimed in claim 17, characterized in that the organic hydroperoxide is ethylbenzene hydroperoxide.

19. A process according to claim 1 for reacting one or more olefinic compounds with one or more organic hydroperoxides so as to produce one or more oxirane compounds, substantially as hereinbefore described with particular reference to the non-comparative parts of the Examples.

20. Oxirane compounds whenever prepared by means of a process as claimed in any one of the preceding claims.

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